A Simple Road for the Transformation of Few-Layer Graphene into MWNTs

Quintana, Mildred; Grzelczak, Marek; Spyrou, Konstantinos; Calvaresi, Matteo; Bals, Sara; Kooi, Bart; Van Tendeloo, Gustaaf; Rudolf, Petra; Zerbetto, Francesco; Prato, Maurizio

Published in:
Journal of the American Chemical Society

DOI:
10.1021/ja303131j

Publication date:
2012

Supporting Information

for

A Simple road for the transformation of few-layer graphene into MWNTs

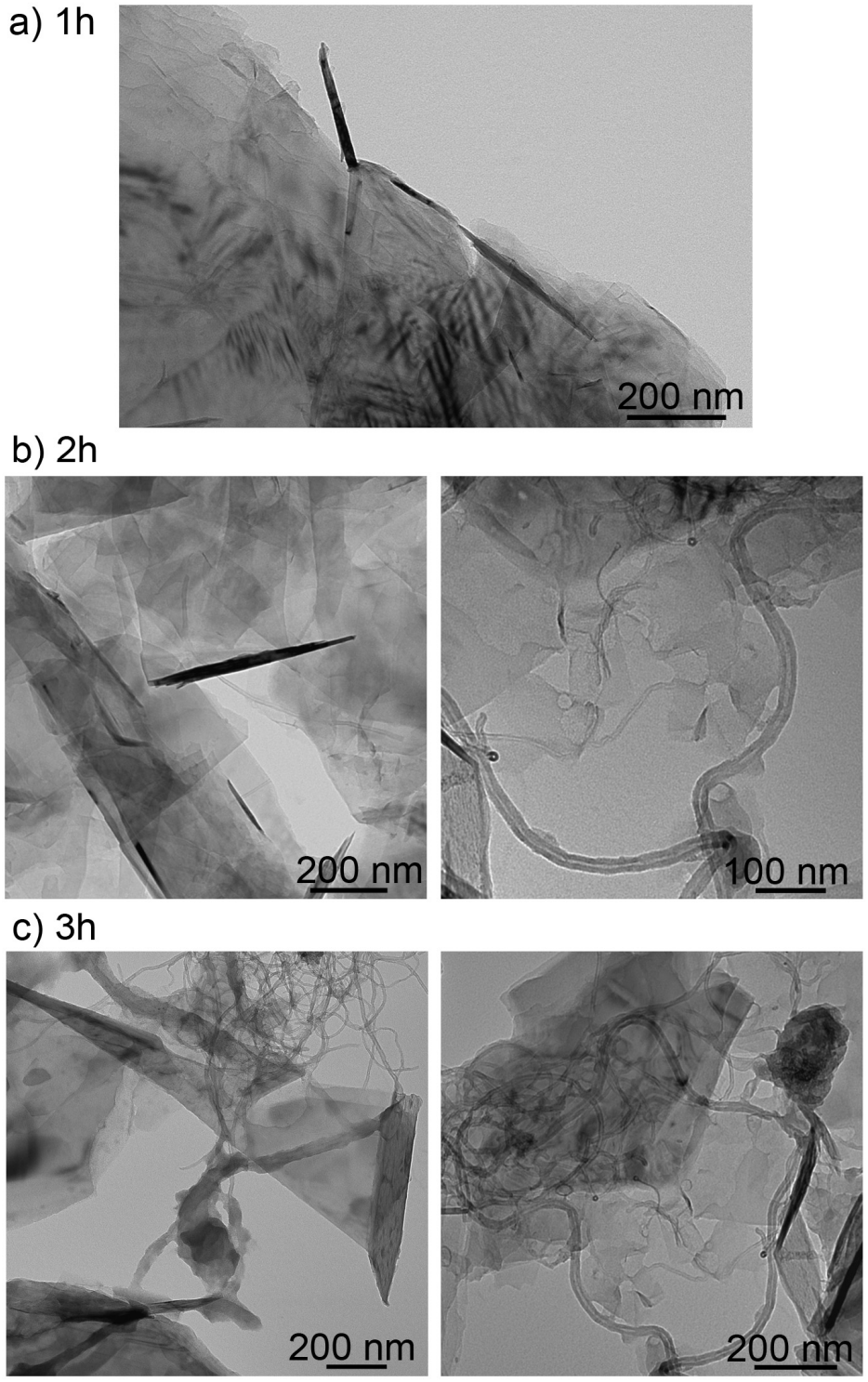
Mildred Quintana,[1] Marek Grzelczak,[1] Konstantinos Spyrou,[2] Matteo Calvaresi,[3] Sara Bals,[4] Bart Kooi,[2] Gustaaf van Tendeloo,[4] Petra Rudolf [2] Francesco Zerbetto[3] and Maurizio Prato[1]

1. Center of Excellence for Nanostructured Materials (CENMAT) and INSTM, unit of Trieste, Dipartimento di Scienze Chimiche e Farmaceutiche, University of Trieste, Piazzale Europa 1, I-34127 Trieste, Italy

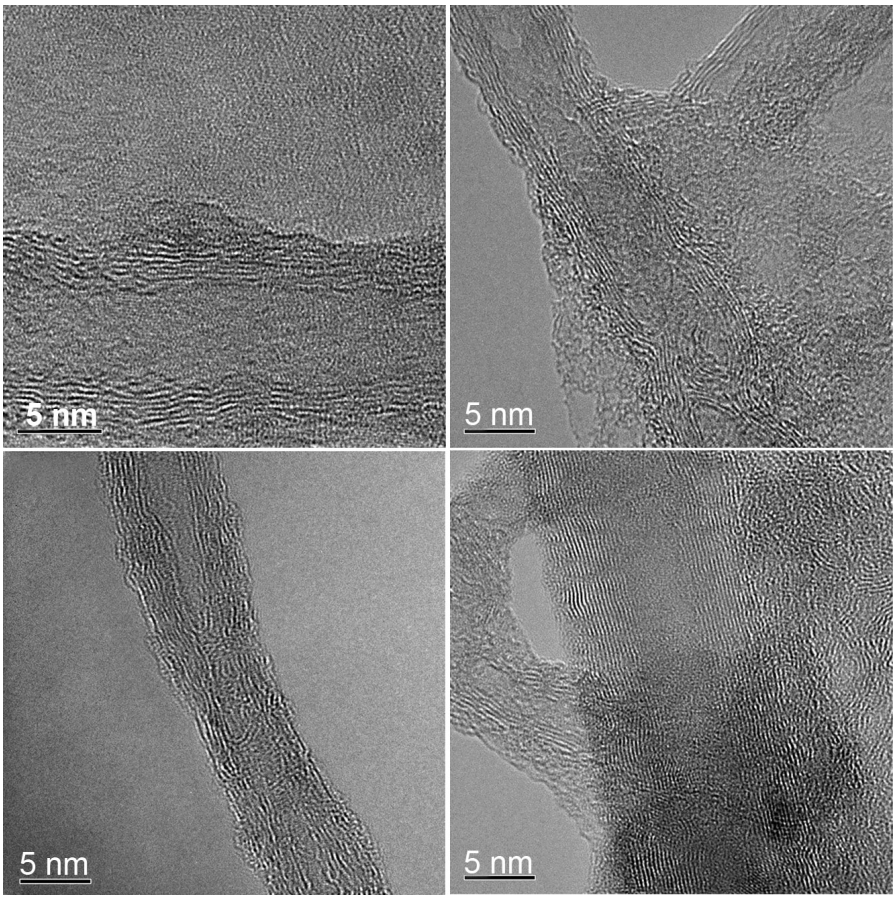
2. Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, NL-9747AG Groningen, The Netherlands

3. Dipartimento di Chimica "G. Ciamician", Università di Bologna, V. F. Selmi 2, 40126 Bologna, Italy

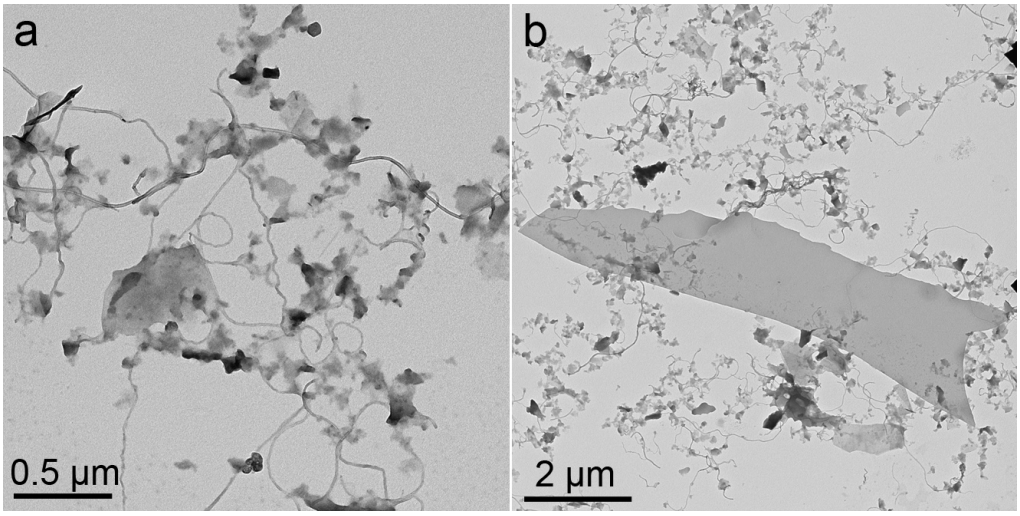
4. EMAT, University of Antwerp, Groenenborgerlaan 171, B-2020 ANTWERP, Belgium



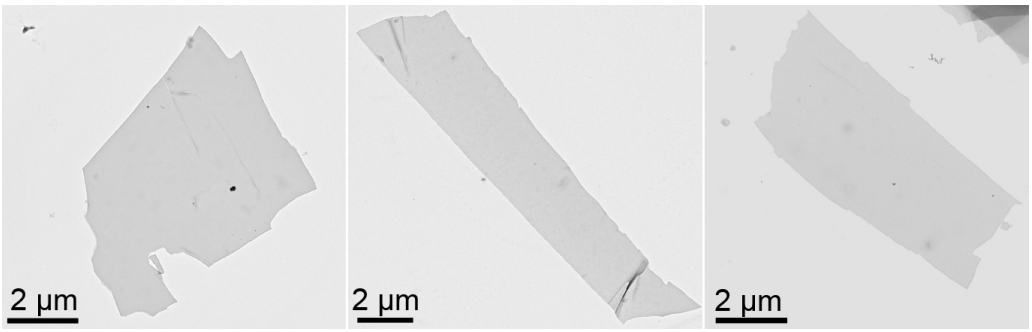
SI-1. MWNT formation on the edges of graphene layers. Evolution during the time is shown.



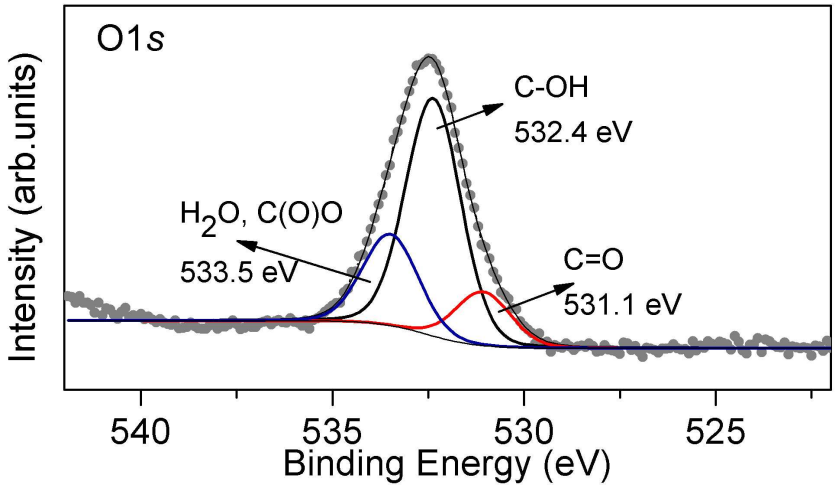
SI-2. HR-TEM of graphene edges and MWNTs formation.



SI-3. MWNTs produced by the addition on **Fc-CHO** mixed with graphene layers.

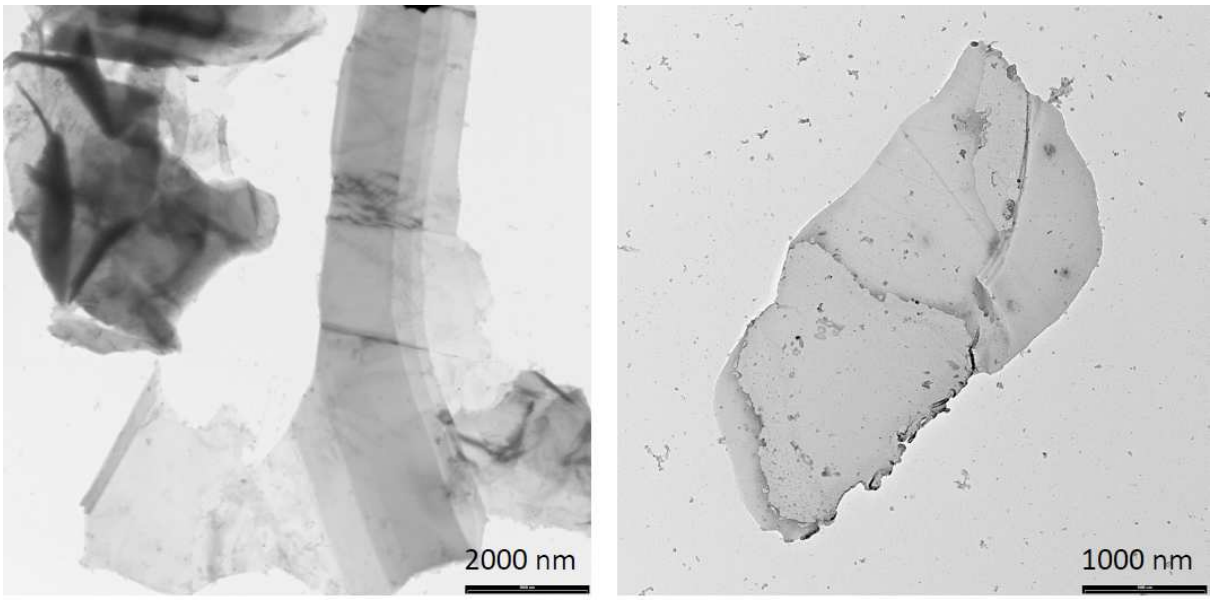


SI-4. G-Fc-CHO

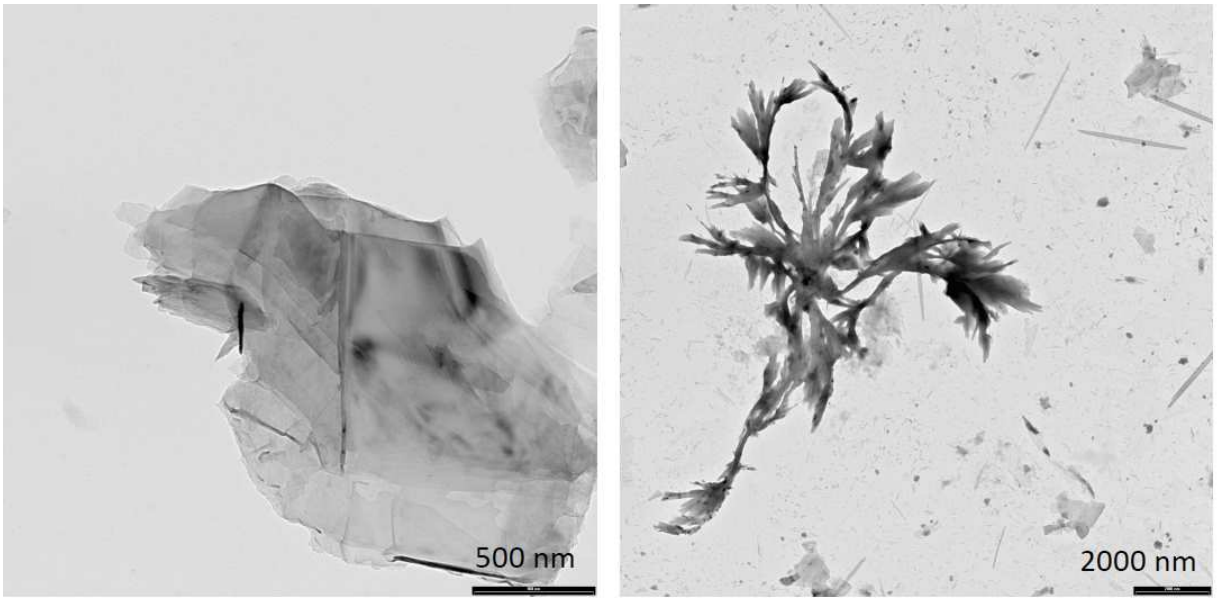


SI-5. O 1*s* peak of **D-Fc-CHO**

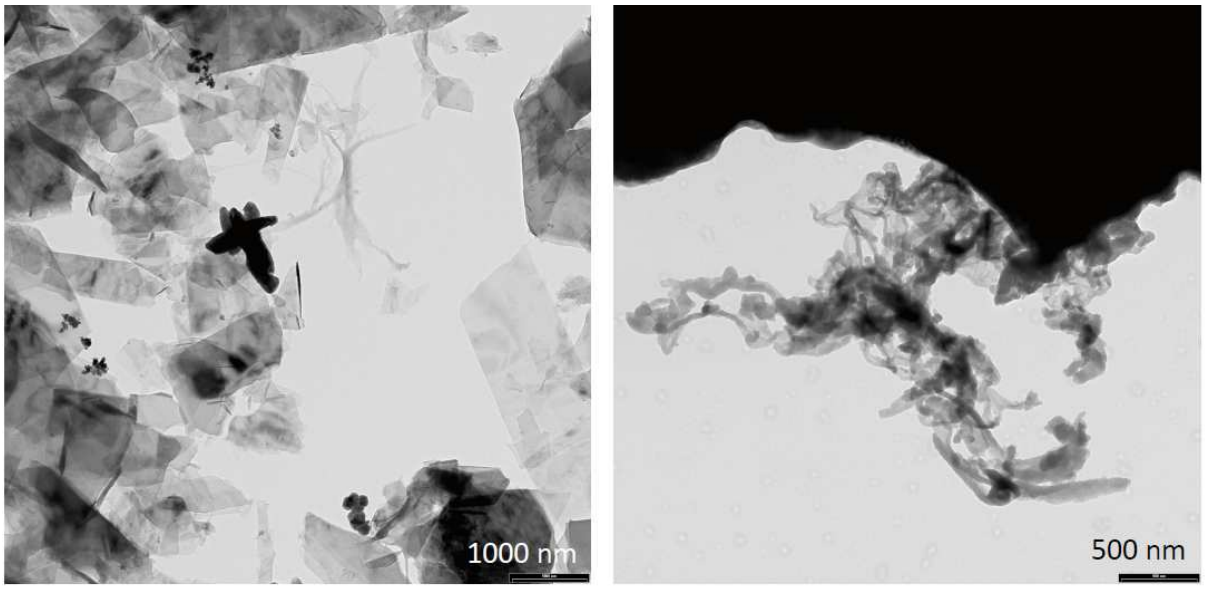
Control experiments preparation. **G-1** dispersion was used as starting material for the control experiments. As control experiment, we performed a 3 h sonication of **G-1** adding (i) Fc, (ii) benzaldehyde, (iii) Fc together with benzaldehyde, (iv) Fc-COOH, and (v) $FcCON(CH_3)_2$. The product was copiously washed by filtration with fresh DMF in order to remove antioxidant and by-product molecules. Samples were re-dispersed in a bath ultrasonicator (few seconds) in 10 ml of fresh DMF. Centrifugation of all dispersions was carried out at 3000 rpm during 30 min. Two liquid fractions, of 5 ml each, of the **D-Fc-CHO** dispersion were collected and analyzed.



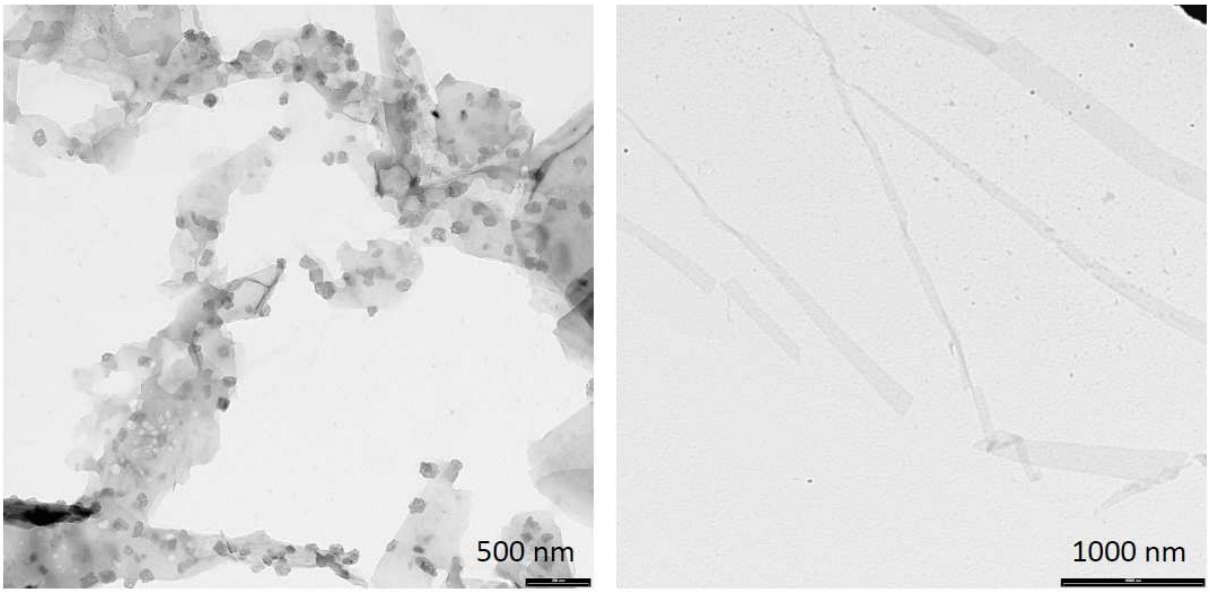
SI-6. Control experiment Fc



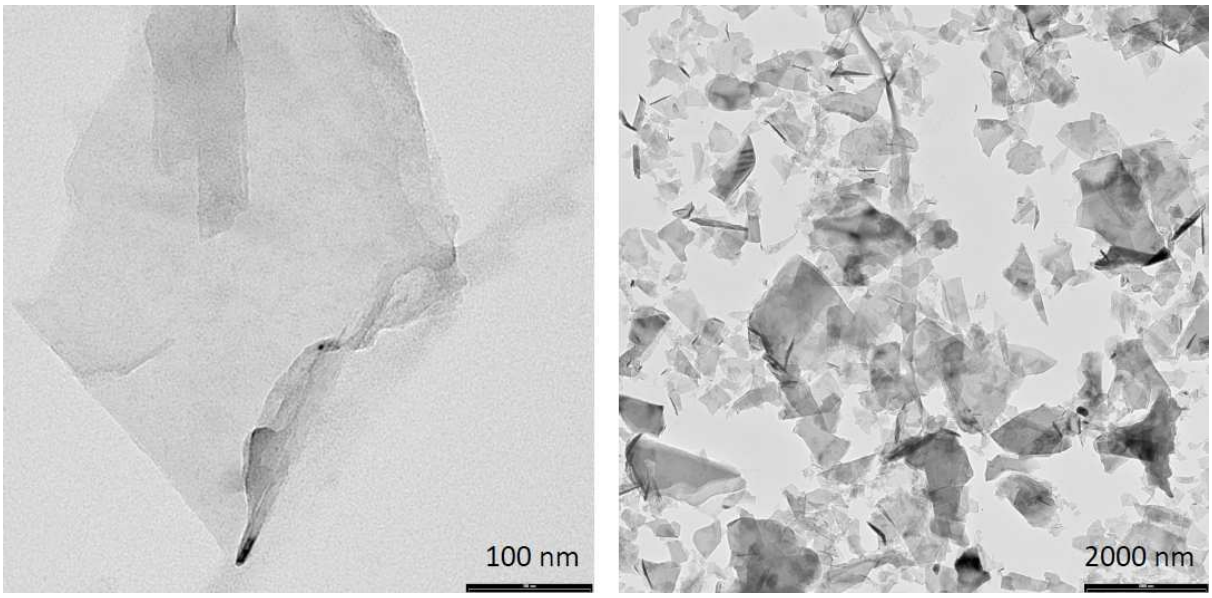
SI-7- Control experiment by adding benzaldehyde.



SI-8. Control experiment by adding Fc and benzaldehyde.



SI-9. Control experiment by adding Fc-COOH



SI-10. Control experiment by adding Fc-CON$(CH_3)_2$.

Molecular Mechanics and Molecular Dynamics calculations for an increasing number of Fc-CHO molecules deposited on the nanoribbon obtained by unzipping a (8,8) CNT

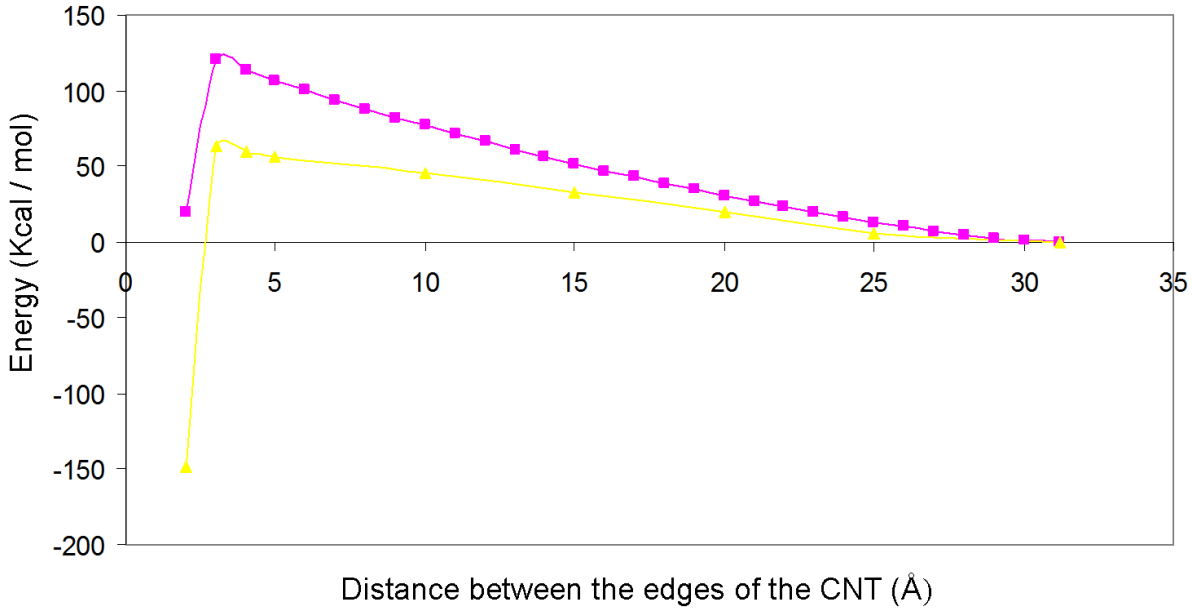
To locate the minimum energy path (MEP) for the rolling up of the graphene nanoribbon in the absence or in the presence of a diverse number of Fc-CHO molecules (Fig SI-11) we carried out different molecular dynamics simulations constraining the distance between the two edges of the nanoribbon.

To avoid that the systems remain trapped in local minima, we employed a high temperature quenched molecular dynamics protocol where the system is first heated from 0 to 600K in 100 ps. Then, a trajectory of 10 ns is carried out at constant temperature (600 K). The RATTLE algorithm constrained the stretching of bonds with hydrogen atoms and allowed for a timestep of 2 fs. The coordinates of the structures were saved every 10 ps for a total of 1000 conformations that were used in further minimizations. Each structure was energy minimized until the root mean square of the gradient was less than 0.01 kcal mol^{-1}.

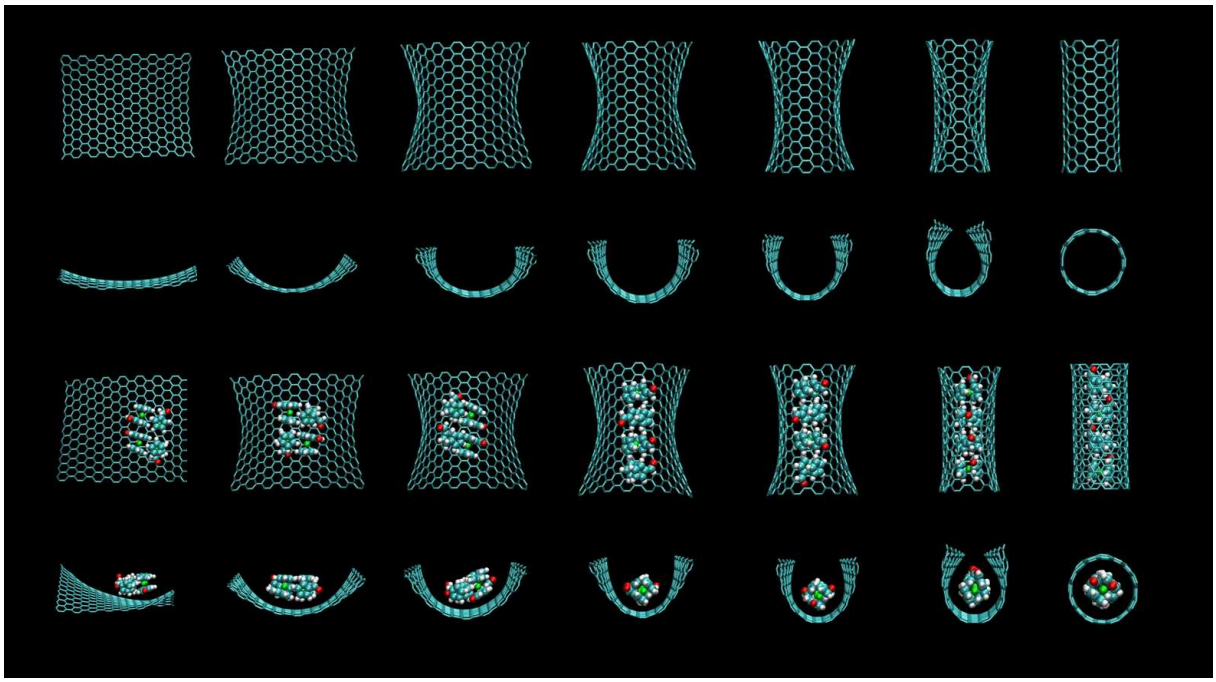
To describe the structure and energetics of the system, we employed Brenner potential for nanoribbon/nanotube and MM3 potential for Fc-CHO and graphene/NT-Fc-CHO interactions, a well tested protocol using a modified version of Tinker.[1]

Table SI-1. Energy barrier for a SWNT (8,8) rolling up with different number of Fc-CHO molecules.

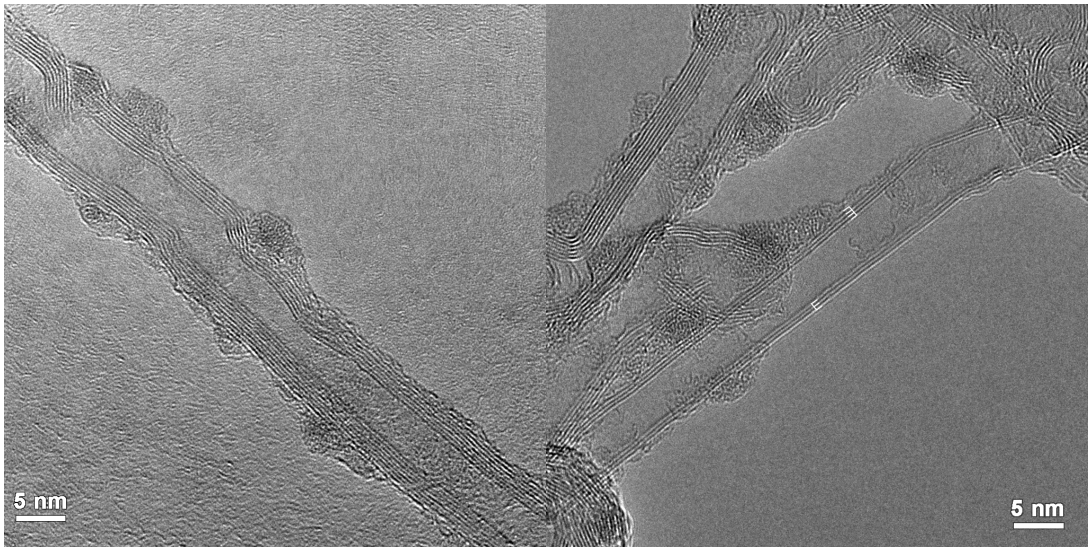
N° of Fc-CHO molecules	Energy barrier for a SWNT (8,8) rolling	Stabilization energy of the Fc-CHO molecule (Kcal mol^{-1})
0	120.3	
1	102.5	17.8
2	86.0	16.5
3	72.0	14.0
4	63.3	8.7



SI-11. Minimum Energy Path (MEP) for the rolling up of the graphene nanoribbon in the absence (purple line) and in the presence of four Fc-CHO molecules (yellow line).



SI-12. Representative snapshots during rolling up of the graphene nanoribbon in the absence and in the presence of four Fc-CHO molecules.



SI-13. MWNTs after annealing treatment.

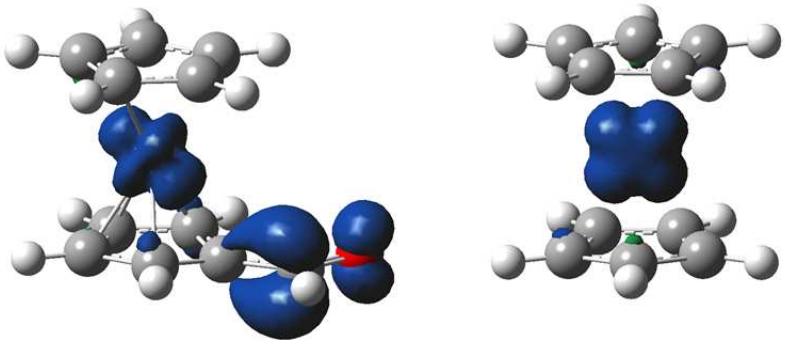
Calculation of the Electron affinities (Eas)

The computations reported in table SI-2 were performed with the Gaussian09[2] series of programs. The geometry of the various critical points was fully optimized with the gradient method available in Gaussian 09 at the DFT level using the M06 functional[3] and the 6-31g** basis set.[4] Single point calculation were then carried out using AUG-cc-PVTZ basis set on the previously optimized geometries.[5] Solvent effect (DMF, $\varepsilon = 37.219$) was taken in account during optimization and single point calculations using the Polarizable Continuum Model (PCM) in the integral equation formalism variant (IEFPCM).[6] The solute cavity was built up using the UFF radii,[7] which place a sphere around each solute atom, with the radii scaled by a factor of 1.1.

The electron affinities (Eas) were calculated as the energy difference between anionic optimised structure and neutral optimised one.

Table SI-2. Electron affinities (Eas).

Molecule	EA (kcal/mol)
Fc-CHO	-50.0
Fc-COOH	-44.4
Fc-CON$(CH_3)_2$	-32.0
Fc	-31.5
Benzaldehyde	-26.6



SI-14. Isosurfaces spin densities of Fc-CHO (left) and Fc (right) radical molecules plotted using an isovalue of 0.004 ea_0^{-3}.

1) Plank, W.; Pfeiffer, R.; Schaman, C.; Kuzmany, H.; Calvaresi, M.; Zerbetto, F.; Meyer, J. *ACS Nano*, **2010**, *4* , 4515–4522.

2) Gaussian 09, Revision **A.02**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

3) Zhao, Y.; Truhlar, D. *Theor. Chem. Acc.,* **2008***, 120*, 215-241.

4) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.*, **1984**, *80*, 3265–3269.

5) Dunning Jr., T. H. *J. Chem. Phys.*, **1989**, *90*, 1007-1023.

6) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.*, **2005**, *105*, 2999–3093.

7) Rappè, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard III, W. A.; Skid, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024–10039.